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BODY RESTORATION PARTS MADE OF TITANIUM OR TITANIUM-BASED ALLOYS AND SURFACE TREATMENT THEREOF

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BODY RESTORATION PARTS MADE OF TITANIUM OR TITANIUM-BASED ALLOYS AND SURFACE TREATMENT THEREOF

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Claims

1. A body restoration part made of titanium or titanium-based alloys furnished with random micro fine pits having mean pore size of 1-10 μm and mean depth of 0.5-5 μm from acid

treatment of at least the surface of the imbedding portion of the body restoration part made of titanium or titanium-based alloys.

2. A surface treatment method of the body restoration part made of titanium or titanium-based alloys described in Claim 1, in that said acid treatment comprises pre-treatment of the surface of the aforementioned imbedding portion by immersing in 1-6 wt% aqueous hydrofluoric acid (HF) solution for 30 sec-3 min, followed by post-treatment immersion in a mixed aqueous solution of 1-6 wt% aqueous hydrofluoric acid and 1-10 wt% hydrogen peroxide (H_2O_2) for 10-60 sec.

Detailed explanation of the invention

Technical application field

This invention pertains to body restoration parts made of titanium or titanium-based alloys in the dental or surgical field, particularly for improving implant parts such as artificial joints, bone connecting parts, artificial bone, artificial dental roots and dentures.

Prior art

The initial binding property of the surface of the aforementioned restoration parts imbedded in the body and biological tissue varies with the surface properties of the parts. Specifically, in case of a smooth surface without any unevenness, the adhesion with the bone is low and the support from the tissues for the parts is insufficient. Conversely, in case of using a rough surface having unevenness, the bone can penetrate and grow in fine pits, achieving a micro-anchoring effect and resulting in strong support of the parts in the bone. Additionally, the required strong initial connecting strength can be obtained at a relatively early stage. For this reason, abrasion treatments of the surface of restoration parts have been conventionally practiced. Specifically, the most commonly exercised techniques include roughening the bare surfaces of the parts by mechanical treatment or by performing plasma flame spray. However, the drawback of the former case includes pollution of the biological tissues by foreign metals deposited on the surface of the parts from the metal tools employed (for cutting, grinding, etc.), and the /2* disadvantage of the latter method is that the operating process is complicated and the cost is high. Japanese Kokai Patent Application No. Sho 55[1980]-120864 proposed furnishing ultrafine pits of 10 nm-1000 nm (0.01-1 μm) on the surface of metal parts for body restoration in an attempt to address the aforementioned drawbacks, but the technique for forming such ultrafine pits is extremely tedious and the cost is very high, while the adhesion to the tissue cells is not always sufficient, so that the problems are hardly solved.

* [Numbers in the right margin indicate pagination of the original text.]

Problems to be solved by the invention

The present invention was undertaken to address and eliminate all of the aforementioned drawbacks by realizing the necessity of preparing rough surfaces having excellent initial surface bonding of the cells in order to establish micro-anchoring effect between the surfaces of body restoration parts made of titanium or titanium-based alloys and the bone tissues. Additionally, the technique for preparing the rough surface must be simple and low cost and have a good production property so that it can be rendered as a surface treatment method for body restoration parts with good control of the surface roughness.

Means to solve the problems

The present invention pertains to a body restoration part made of titanium or titanium-based alloys furnished with random pits having mean pore size of 1-10 μm and mean depth of 0.5-5 μm from acid treatment of at least the surface of the imbedding portion of the body restoration part made of titanium or titanium-based alloys. The present invention also pertains to a surface treatment method of the body restoration part made of titanium or titanium-based alloys, in that said acid treatment comprises pre-treatment of the surface of the aforementioned imbedding portion by immersing in 1-6 wt% aqueous hydrofluoric acid (HF) solution for 30 sec-3 min, followed by post-treatment immersion in a mixed aqueous solution of 1-6 wt% aqueous hydrofluoric acid and 1-10 wt% hydrogen peroxide (H_2O_2) for 10-60 sec.

Effect

The aqueous hydrofluoric acid (HF) solution utilized in the pre-treatment can sufficiently clean the pollution of the oxide film made by foreign metals incurred during surface finishing process on the surface of the body restoration part made of titanium or titanium-based alloys and helps furnish numerous micro fine pits having mean pore size of 1-10 μm and mean depth of 0.5-5 μm at specific conditions to be described later. Also, by adjusting the concentration and time of immersion, the aforementioned pore size and depth can be varied and the surface roughness can be regulated. The HF concentration is set at 1-6 wt% because if it is less than 1 wt%, the pore size cannot reach 1 μm, while if it is more than 6 wt%, the pore size will be larger than 10 μm. If the mean pore size is smaller than 1 μm, the bonding force of the cells is poor while if it is larger than 10 μm, the cells will adhere to the pit bottom while having little adhesion to the ridge portion because the pore size may become larger than the size of the tissue cells (the size is said to be 10-100 μm). The mean depth is set at 0.5-5 μm because if it is less than 0.5 μm, the anchoring effect between the bone and the restoration parts is insufficient while if it is greater than 5 μm, sharp edges or pointed ends will form on the ridgelines of the pits

which can irritate the tissues (may develop to become a trigger for cancer). The time of immersion is set at 30 sec-3 min because if it is less than 30 sec, the depth of the pits is too shallow and the cleaning of the polluted layer during the pretreatment may be insufficient while if it is greater than 3 min, the depth of the pits is too deep so that many sharp edges or pointed ends will form on the ridgelines of the pits, as described earlier.

The post-treatment immersion in mixed aqueous solutions of HF and H_2O_2 is to smooth the sharp edges or pointed ends formed on the ridgelines of the micro fine pits generated during the pretreatment. As to be described later, replacing the mixed aqueous solution with aqueous H_2O_2 solution solely resulted in no smoothening of the sharp edges or pointed ends. The concentration of the aqueous H_2O_2 solution is set at 1-10 wt% because if it is less than 1 wt%, the same result as using HF solely is obtained, that is, the elimination of the sharp edges or pointed ends is insufficient, while if it is more than 10 wt%, the pore size is greatly enlarged, facilitating the formation of sharp edges or pointed ends. The time of immersion is set at 10-60 sec because if it is less than 10 sec, the effect is insufficient, while if it is longer than 60 sec, sharp edges or pointed ends will appear. /3

Application examples

The application examples of the present invention are shown in the following Table 1, together with comparative examples and experimental examples.

Table 1

(1) 試料No.及び属性	(2) 表面処理内容	(3) 表面粗さ測定結果 測定距離0.25mm Rz(μm)	(4) Rmax(μm)	測定距離0.80mm Rz(μm)	Rmax(μm)	(5) 電子顕微鏡観察結果(なお数値は凹みの孔径(差し渡し内径)を示す)	(6) 目視観察結果
(7) 比較例1	表面処理前の試料 (8)	0.3	0.6	0.6	2.1	(9) 表面に打痕、クレバス、あるいは削られた穴がある。	一見鏡面(多少打痕有り) (10)
比較例2	4%HF 1分間 後処理なし (11)	1.3	2.0	2.4	3.5	2μm~3μmのピットが多く見られるが、シャープエッジや尖鋭とげがある。 (12)	銀灰色(やや黄ばみ) (13)
(14) 実施例1	4%HF 30秒間、4%HF+4%H₂O₂ 後処理 15秒間 (15)	1.4	2.5	2.5	3.2	2μm~5μmのピットが多く見られ、シャープエッジは若干あるが尖鋭とげはない。 (16)	銀白色 (17)
実施例2	4%HF 1分間、4%HF+8%H₂O₂ 後処理 15秒間 (18)	1.3	2.6	2.4	3.3	(19) 2μm~5μmのピットが多く見られ、シャープエッジや尖鋭とげはない。	銀白色
実施例3	4%HF 2分間、4%HF+8%H₂O₂ 後処理 15秒間 (20)	1.8	3.2	2.8	4.8	(21) 2μm~10μmのピットが多く見られ大きなピットの中に1~3μmの小さなピットが見られる。シャープエッジ、尖鋭とげはない	銀白色
実施例4	2%HF 1分間、4%HF+8%H₂O₂ 後処理 15秒間 (22)	1.4	3.4	2.4	3.4	(23) 2μm~3μmのピットが多く見られシャープエッジが若干みられる。	銀白色
実施例5	8%HF 1分間、4%HF+8%H₂O₂ 後処理 15秒間 (24)	2	4.2	3	4.5	2μm~10μmのピットが多く見られ、大きなピットの中に2~5μmの小さなピットが見られる。シャープエッジ、尖鋭とげは若干みられる。 (25)	銀白色
(26) 実験例1	4%HF 1分間、3%H₂O₂ (27) 後処理 1分間	1	1.6	2	3.3	(28) 0.5μm~4μmのピットが多く見られるが、シャープエッジがある。尖鋭とげもある。	銀灰色(やや黄ばみ)
実験例2	4%HF 1分間、8%H₂O₂ (29) 後処理 15秒間	1.1	1.9	2.6	3.6	(28) 0.5μm~4μmのピットが多く見られるが、シャープエッジがある。尖鋭とげもある。	銀灰色(やや黄ばみ) (13)

Notes

1. The testing distance is the distance with respect to the testing direction along the axis of the sample.

2. Rz is the mean depth of 10 pits including 5 pits and 5 ridges along the testing distance.
3. Rmax is the maximum depth of the pits along the testing distance.
4. Comparative Examples 1 and 2 were samples of prior art.
5. Experimental Examples 1 and 2 were the samples using H_2O_2 solely for post-treatment.
6. The pore sizes of the pits were calculated from the electron microscope pictures.

Key:
1 Sample No. and type
2 Content of surface treatment
3 Test result of surface roughness
4 Test distance
5 Results of observation by electron microscope (in this respect, the numbers show the pore size of the pits (inner diameter))
6 Results of eye observation
7 Comparative example
8 Sample before surface treatment
9 The polished surface showed pounding marks, crevices, or obscured openings.
10 Superficially smooth surface (with some pounding marks)
11 4% HF for 1 min, no post-treatment
12 Many 2 μm-3 μm pits were observed but there were sharp edges and had pointed ends
13 Silver gray color (with very slight pale yellow)
14 Application example
15 4% HF for 30 sec, post-treatment with 4% HF + 8% H_2O_2 for 15 sec
16 Many 2 μm-5 μm pits were observed, with some sharp edges but no pointed ends
17 Silver white color
18 4% HF for 1 min, post-treatment with 4% HF + 8% H_2O_2 for 15 sec
19 Many 2 μm-5 μm pits were observed, but no sharp edges or pointed ends
20 4% HF for 2 min, post-treatment with 4% HF + 8% H_2O_2 for 15 sec
21 Many 2 μm-10 μm pits were observed with small pits of 1-3 μm in large pits, but no sharp edges or pointed ends
22 2% HF for 1 min, post-treatment with 4% HF + 8% H_2O_2 for 15 sec
23 Many 1 μm-3 μm pits were observed with some sharp edges
24 8% HF for 1 min, post-treatment with 4% HF + 8% H_2O_2 for 15 sec
25 Many 2 μm-10 μm pits were observed with small pits of 2-5 μm in large pits, with some sharp edges or pointed ends
26 Experimental example
27 4% HF for 1 min, post-treatment with 8% H_2O_2 for 1 min
28 Many 0.5 μm-4 μm pits were observed with sharp edges as well as pointed ends
29 4% HF for 1 min, post-treatment with 8% H_2O_2 for 15 sec

The results in Table 1 are explained in accordance with the sequence of Table 1 by /4
referring to the electron microscope pictures (hereafter known simply as the pictures) utilized as the accompanied figures:

(1) As shown in Picture 1, the sample of Comparative Example 1 with the original finished surface having no treatment showed short pounding marks, crevices (obscured pits in pictures not shown), thus is not suitable for application taking into consideration the adhesion strength of the binding tissues.

(2) As shown in Picture 2, the sample of Comparative Example 1 [sic; 2] with HF treatment showed many pits from acid corrosion, but there were sharp edges formed on the pit edges (on the white ridgelines), thus is not suitable for application taking into consideration the irritation to the tissues.

(3) As shown in Picture 3, the sample of Application Example 1 with 1/2 the time of treatment with HF compared with the Comparative Example 2, followed by immersing in the mixed aqueous solution of HF + H_2O_2, had most of the sharp edges eliminated (the white ridgelines were fading) while there were no pointed ends.

(4) As shown in Picture 4, the sample of Application Example 2 having the same HF treatment condition as Comparative Example 2 but followed by treatment with the aforementioned mixed aqueous solution showed the best result without sharp edges or pointed ends.

(5) As shown in Picture 5, the sample of Application Example 3 with twice the time of HF treatment compared with Application Example 2, followed by the same post-treatment condition as in Application Example 2, showed about 2-fold enlargement of the pore size with small pits (1-3 μm) observed in large pits, but no sharp edges or pointed ends were observed.

(6) As shown in Picture 6, the sample of Application Example 4 treated with 1/2 the HF concentration compared with the previous Application example, followed by the same post-treatment with the mixed aqueous solution showed little change in the pore size with some sharp edges and pointed ends, but the degree is negligible.

(7) As shown in Picture 7, the sample of Application Example 5 treated with twice the HF concentration compared with Application examples 1-3, followed by the same post-treatment with the mixed aqueous solution, showed about the same result as in Application Example 4.

(8) As shown in Picture 8, the sample of Experimental example 1 using aqueous H_2O_2 solution for post-treatment with 1 min of post-treatment time showed reduced pore size while many sharp edges and pointed ends appeared.

(9) As shown in Picture 9, the sample of Experimental example 2 treated with the same post-treatment solution as in Application Example 1 but with 15 sec of post-treatment time showed about the same result as in Application Example 1.

(10) The pore sizes (surface roughness) of the pits could be varied in Application examples 1-5 by changing the HF concentration or the immersion time.

Summarizing the aforementioned results further:

a) A smooth surface treated with HF shows acid corrosion and forms many pits but the ridgelines of the aforementioned pits are eliminated by subsequent post-treatment with mixed aqueous solution of HF and H_2O_2, yet if the HF concentration is too low, the sharp edges and pointed ends may return.

b) In case the aqueous post-treatment solution contains H_2O_2 solely without HF, for some reason the sharp edges and pointed ends cannot be eliminated.

c) The pore size of the pits can be varied by changing the HF concentration and treatment time.

d) The silver-gray color of the material base turns to a nice silver white color by using the aqueous post-treatment solution of the present invention.

Effect of the present invention

As clearly shown in the aforementioned explanation, the present invention provides body restoration parts made of titanium or titanium-based alloys characterized by having excellent bonding strength and good appearance by furnishing them with random micro fine pits having mean pore size of 1-10 μm and mean depth of 0.5-5 μm resulting from acid treatment of the surface of the imbedding portion, in that the acid treatment is performed with hydrofluoric acid solution as pretreatment to induce acid corrosion, followed by subsequent post-treatment using a mixed aqueous solution of the same hydrofluoric acid and hydrogen peroxide, and there are many advantages because the method is simple with good production property while the surface roughness can be easily varied by changing the HF concentration or treatment time.

Brief explanation of the figures /6

Photos 1-9 are electron microscope photos illustrating the surface state of the body restoration part corresponding to the order of the samples in Table 1

Figure 1 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Comparative Example 1 without treatment on the smooth surface, Figure 2 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Comparative Example 2, Figure 3 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Application Example 1, Figure 4 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Application Example 2, Figure 5 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Application Example 3, Figure 6 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Application Example 4, Figure 7 is the electron microscope picture (x

2000) showing the crystalline structure of the surface of the sample of Application Example 5, Figure 8 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Experimental example 1 and Figure 9 is the electron microscope picture (x 2000) showing the crystalline structure of the surface of the sample of Experimental Example 2.

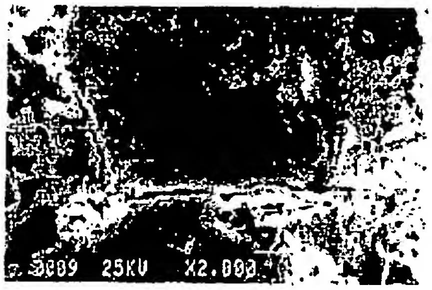

Photo 1

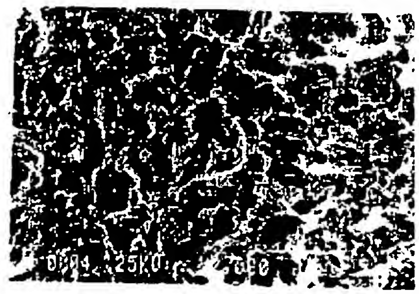

Photo 2

Photo 3

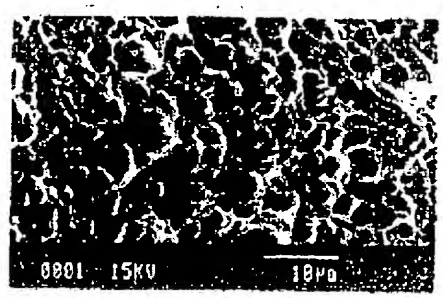

Photo 4

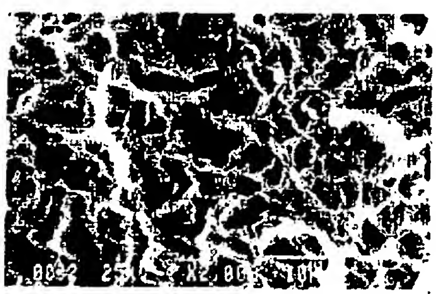

Photo 5

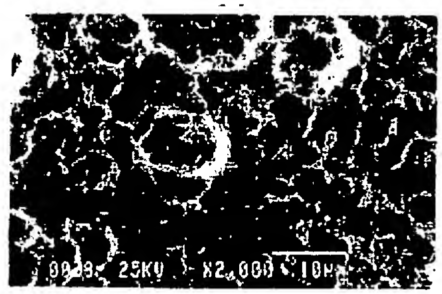

Photo 6

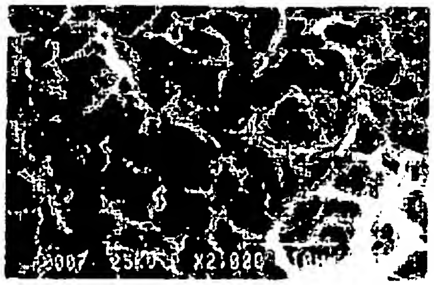

Photo 7

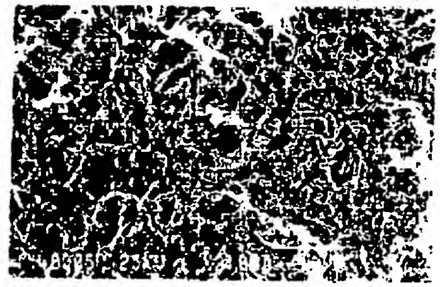

Photo 8

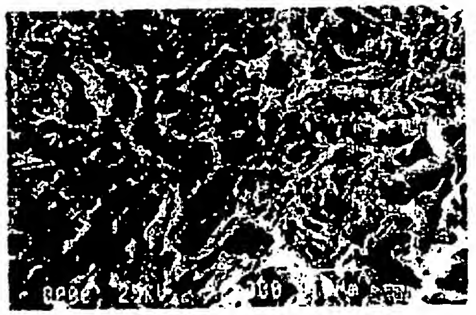

Photo 9